DFT Based Calculations Of Energies And Densities Of Frontier Orbital Of Lewis Acids And Lewis Bases And Their Interaction

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ABSTRACT

Energies and densities of number of metal halides and organic bases have been evaluated by DFT-PW 91 method, in conjunction with DZVP basis on Cache pro software. The energy values have mainly been used to prepare scale of hardness of metal halides and organic bases. The density values have been used to identify the reactive sites in different molecules. The metal ligand interaction and the stability of metal-ligand bond have been studied with the help of LUMO density values of acceptor and HOMO density values of donor molecules. The stability has been expressed by the difference in two densities by ΔLH in non transition metal halides and by $\Delta LH + IP$ in transition metal halides. The stability of metal-ligand bond has also been related with transfer of charge DN and lowering of energy DE. The results obtained by DFT calculations are well related with the result obtained by Klopman equation.   © 2007 Trade Science Inc. - INDIA

INTRODUCTION

Klopman[1] developed a quantum mechanical equation for calculation of quantitative values of softness of acid and base ions and derived the reactivity by the difference in softness values of acid and base ions. By simple modification of known methods[2-5] Singh et al calculated the values of ionization potential, charge and radius of atom for neutral molecules, and solved the Klopman equation for neutral Lewis acids and bases, and developed matching between them in terms of $\Delta E_{nm} \pm$ and their relationship to the stability of metal-ligand bond[6]. The application of density functional theory (DFT)[7], has given a new concept to chemical system. This concept focuses on the one electron density function instead of wave function[8]. For every chemical system there is a quantity μcalled the electronic chemical potential. A chemical system is an atom, molecule, ion or radical or several such unit in a state of interaction. Recent work based

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on density functional theory has developed the concept of absolute electronegativity, χ, and absolute hardness η[9,10]. The definitions are

$$\chi = -E / N_z = -\mu \tag{1}$$
$$\eta = \tfrac{1}{2} E / N_z^2 \tag{2}$$

Where E is the electronic energy of a molecule, atom, or ion, N is the number of electrons, and Z is a fixed set of nuclear charges. The absolute electronegativity is also equal to the electronic chemical potential, m, with change in sign. The operational (and approximate) definitions are

$$\chi = \tfrac{1}{2}(I + A) \tag{3}$$
$$\eta = \tfrac{1}{2}(I - A) \tag{4}$$

Where I is the ionization potential, and A is the electron affinity. The absolute electronegativity is the same as the Mulliken value.

Klopman based his concept on charge and frontier orbital controlled chemical reactions of perturbation theory. Parr and Yang[11], reconciled DFT with the frontier orbital theory of chemical reactivity. Since this theory is very successful, it is important to examine the correlation of this theory with that of the Klopman approach. We in this paper have made DFT calculations and have examined the relationship with the results obtained by Klopman equation.

MATERIALS AND METHOD

Metal halides of transition and non transition metals have been used as Lewis acids and various organic compounds have been used as Lewis bases. For metal-ligand interaction study, the 3D modeling, and geometry optimization of all the compounds have been done with the help of CAChe software, using DFT-B88-PW91 method in conjunction with DZVP basis set. The values of various descriptors, charge, electron density, eigen values of frontier orbital, absolute hardness and electronegativity etc., of Lewis acid and Lewis bases have been evaluated by solving the equation 1-8. When Lewis acid reacts with Lewis base there is a shift of electron from the Lewis base to Lewis acid, until the chemical potentials of both become equal. The condition of equilibrium is that the chemical potential, μ_A and μ_B, become equal. This leads to shift in charge, ΔN, from less electronegative base (B) to more electronegative acid (A).

$$\Delta N = (\chi^{\circ}_A - \chi^{\circ}_B) / 2(\eta_A + \eta_B) \tag{5}$$

Electron transfer leads to an energy lowering given by equation 6.

$$\Delta E = (\chi^{\circ}_A - \chi^{\circ}_B)^2 / 4(\eta_A + \eta_B) \tag{6}$$

In equation 5 and 6 the electronegativity difference derive the electron transfer, and the sum of hardness parameters inhibits it. The hardness is the resistance of the chemical potential to change in the number of electrons. That is,

$$2\eta = (\delta\mu/N)_z \tag{7}$$

The chemical potential and the absolute electronegativity are molecular properties and not orbital properties. According to Koopman's[7] theorem the I is simply the eigen value of HOMO with change of sign and A is the eigen value of LUMO with change of sign, hence the equation-4 can be written as-

$$\eta = 1/2(\varepsilon LUMO - \varepsilon HOMO) \tag{8}$$

RESULTS AND DISCUSSION

Frontier molecular orbital energies

Energies of HOMO and LUMO are very popular quantum mechanical descriptors. It has been shown[12] that these orbitals play a major role in governing many chemical reactions, and are also responsible for charge transfer complexes[13]. The treatment of the frontier molecular orbitals separately from the other orbitals is based on the general principles governing the nature of chemical reactions[14]. The energy of the HOMO is directly related to the ionization potential and characterizes the susceptibility of the molecule towards attack of electrophiles. The energy of LUMO is directly related to the electron affinity and characterizes the susceptibility of the molecule towards attack of nucleophiles. The concept of hard and soft nucleophiles and electrophiles has been also directly related to the relative energies of the HOMO and LUMO orbitals. Hard nucleophiles have a low energy HOMO, soft nucleophiles have a high energy HOMO, hard electrophiles have a high energy LUMO and soft electrophiles have a low energy LUMO[15]. HOMO-LUMO gap is an important stability index[16].

$$\varepsilon LUMO - \varepsilon HOMO = \text{energy gap} \tag{9}$$

Absolute hardness η is equal to half the value of

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the difference in energy of the LUMO and HOMO [13, 17].

$$\eta = (\varepsilon\,LUMO - \varepsilon HOMO)/2$$

Nucleophiles

The energies of the LUMO and HOMO have been evaluated for a set of organic nucleophiles. The difference in energies of HOMO-LUMO, and value of absolute hardness η, derived from the energy values are presented in TABLE 1.

(i) The values of absolute hardness indicate that amines, amides and ureas are hard bases and the values range between 3.451 for ammonia and 2.503 for tetra methyl urea. It is also prominently evident that phenyl substitution in amines amides and ureas reduce their hard character. The values come down to 1.559 in case of triphenyl amine, to 1.841 in benzamide and to 1.7725 in tetra phenyl urea. This range of hardness is very close to soft range

(ii) The derivatives of pyridine indicate an intermediate status on the scale of hardness. The values are in the range of 2.102 for methyl pyridine to 2.237 for fluoro pyridine. Nitro and iodo substitution reduces the hardness. The values respectively change to 1.452 and 1.935.

(iii) The hardness value in case of thioamide, thioureas and selenoureas are in the range of 0.942 for diethyl thioamide, and 1.752 for tetramethyl thiourea. It is also evident that phenyl substitution makes them softer. The seleno derivatives are softer than thio derivatives. The value in tetra methyl thiourea is 1.752 and the value in the corresponding seleno derivative is 1.385.

Non transition metal halides

The energies of LUMO and HOMO of metal halides and the values of difference between the two energies, the values of absolute hardness are included in TABLE 2. A reference to the table indicates that.

(i) The values of hardness are highest in case of zinc halides and lowest in case of mercury halides. The hardness value for ZnF_2, is 2.752, that of CdF_2 and HgF_2 are 2.324 and 1.978 respectively. The lowest value is seen in case of selenocyanate derivatives in all the cases.

(ii) In case of Sn(IV) halides, the iodide derivative is softer than its bromide and chloride derivatives. Substitution of one phenyl group makes the deriva-

TABLE 1: Absolute hardness values of nucleophiles drawn from eigen values of HOMO and LUMO

Chemical Sample	ε HOMO	ε LUMO	LUMO-HOMO	η
NH_3	-5.694	1.208	-6.902	-3.451
CH_3NH_2	-5.138	1.288	-6.426	-3.213
$(CH_3)_2NH$	-4.795	1.369	-6.164	-3.082
$(CH_3)_3N$	-4.597	1.525	-6.122	-3.061
$(C_2H_5)NH_2$	-5.172	1.405	-6.577	-3.2885
$(C_2H_5)_2NH$	-4.825	1.555	-6.38	-3.19
$(C_2H_5)_3N$	-4.456	1.78	-6.236	-3.118
$PhNH_2$	-4.454	-0.663	-3.791	-1.8955
Ph_2NH	4.504	-1.12	5.624	2.812
Ph_3NH	4.413	-1.295	5.708	2.854
$HCONH_2$	5.759	-0.512	6.271	3.1355
CH_3CONH_2	5.502	-0.286	5.788	2.894
$C_2H_5CONH_2$	-5.433	-0.371	-5.062	-2.531
$HCONHCH_3$	-5.616	-0.49	-5.126	-2.563
$PhCONH_2$	-5.643	-1.961	-3.682	-1.841
NH_2CONH_2	-5.58	0.555	-6.135	-3.0675
$CH_3NHCONH_2$	-5.561	0.233	-5.794	-2.897
$CH_3NHCONHCH_3$	-5.467	0.302	-5.769	-2.8845
$(CH_3)_2NCON(CH_3)_2$	-5.144	-0.138	-5.006	-2.503
$PhNHCONH_2$	-5.287	-0.993	-4.294	-2.147
$Ph_2NCONPh_2$	-5.064	-1.519	-3.545	-1.7725
$HCSNH_2$	-4.813	-1.805	-3.008	-1.504
$HCSNHCH_3$	-4.662	-1.625	-3.037	-1.5185
$HCSNHC_2H_5$	-5.27	-2.504	-2.766	-1.383
$HCSN(C_2H_5)_2$	-4.772	-2.887	-1.885	-0.9425
$HCSNHPh$	-4.992	-2.796	-2.196	-1.098
$HCSNPh_2$	-4.8	-2.863	-1.937	-0.9685
NH_2CSNH_2	-4.999	-1.199	-3.8	-1.9
$(CH_3)_2NCSN(CH_3)_2$	-4.352	-0.849	-3.503	-1.7515
$(C_2H_5)_2NCSN(C_2H_5)_2$	-4.048	-0.799	-3.249	-1.6245
$CH_3NHCSeHNCH_3$	-4.097	-0.836	-3.261	-1.6305
$(CH_3)_2NCSeN(CH_3)_2$	-3.942	-1.173	-2.769	-1.3845
$PhNHCSeHNPh$	-4.072	-1.636	-2.436	-1.218
C_5H_4FN	-6.437	-1.963	-4.474	-2.237
C_5H_4ClN	-6.337	-2.006	-4.331	-2.1655
C_5H_4BrN	-6.172	-2.011	-4.161	-2.0805
C_5H_4IN	-5.875	-2.006	-3.869	-1.9345
$C_5H_4NO_2N$	-6.532	-3.628	-2.904	-1.452
$C_5H_4CH_3N$	-5.694	-1.491	-4.203	-2.1015
PPh_3	-6.353	0.411	-6.764	-3.382
$(CH_3)_3P$	-5.085	0.732	-5.817	-2.9085
AsH_3	-6.516	0.201	-6.717	-3.3585

εHOMO is eigen values of highest occupied molecular orbital; εLUMO is eigen values of lowest unoccupied molecular orbital, LUMO-HOMO is the energy gap, η is the absolute hardness calculated from equation - 7, DFT calculation have been made by DFT PW-91 method in conjunction with DZVP basis set on Cache Pro. Software

tives soft as the value comes down to 0.711, however, substitution of two and three phenyl group makes the derivative comparatively harder. Similarly the methyl substitutions also have the hardening ef-

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TABLE 2 : Absolute hardness values of non-transitional metal halides, drawn from eigen values of HOMO and LUMO.

Chemical Sample	ε HOMO	ε LUMO	LUMO-HOMO	η
ZnF_2	-8.507	-3.003	-5.504	-2.752
$ZnCl_2$	0.88	4.778	-3.898	-1.949
$ZnBr_2$	-7.221	-2.785	-4.436	-2.218
ZnI_2	-6.71	-2.868	-3.842	-1.921
$Zn(NCS)_2$	-6.308	-2.193	-4.115	-2.0575
$Zn(NCSe)_2$	-5.93	-2.302	-3.628	-1.814
CdF_2	-7.902	-3.253	-4.649	-2.3245
$CdBr_2$	-7.011	-3.103	-3.908	-1.954
$Cd(NCS)_2$	-6.107	-3.262	-2.845	-1.4225
$Cd(NCSe)_2$	-5.701	-3.025	-2.676	-1.338
HgF_2	-8.489	-4.533	-3.956	-1.978
HgI_2	-6.711	-3.93	-2.781	-1.3905
$Hg(SCN)_2$	-6.245	-3.236	-3.009	-1.5045
$Hg(SeCN)_2$	-15.154	-15.881	0.727	0.3635
$SnCl_4$	-8.086	-4.5	-3.586	-1.793
$SnBr_4$	-7.27	-4.342	-2.928	-1.464
SnI_4	-6.497	-4.359	-2.138	-1.069
$PhSnCl_3$	-17.838	-19.26	1.422	0.711
Ph_2SnCl_2	-6.445	-2.13	-4.315	-2.1575
Ph_3SnCl	-6.059	-1.422	-4.637	-2.3185
$(CH_3)SnCl_3$	-7.521	-3.308	-4.213	-2.1065
$(CH_3)_2SnCl_2$	-6.869	2.082	-8.951	-4.4755
$(CH_3)_3SnCl$	-6.396	-0.884	-5.512	-2.756
BaF_2	-7.738	-6.105	-1.633	-0.8165
$BaCl_2$	-6.896	-5.517	-1.379	-0.6895
$BaBr_2$	-6.498	-5.276	-1.222	-0.611
BaI_2	-6.013	-5.046	-0.967	-0.4835
BeF_2	-9.514	-1.687	-7.827	-3.9135
$BeCl_2$	-8.06	-1.616	-6.444	-3.222
$BeBr_2$	-7.443	-1.689	-5.754	-2.877
BeI_2	-6.829	-1.809	-5.02	-2.51
CaF_2	-6.966	-2.078	-4.888	-2.444
$CaCl_2$	-7.083	-2.754	-4.329	-2.1645
$CaBr_2$	-6.702	-2.766	-3.936	-1.968
CaI_2	-6.298	-2.844	-3.532	-1.766
MgF_2	-8.121	-2.312	-5.277	-2.6385
$MgCl_2$	-7.611	-2.609	-5.299	-2.6495
$MgBr_2$	-7.112	-2.537	-4.503	-2.2515
MgI_2	-6.612	-2.529	-4.075	-2.0375
SrF_2	-6.258	-1.968	-3.729	-1.8645
$SrCl_2$	-6.657	-2.564	-4.689	-2.3445
$SrBr_2$	-6.375	-2.598	-3.811	-1.9055
SrI_2	-6.045	-2.687	-3.447	-1.7235
LiF	-5.596	-1.327	-2.909	-1.4545
$LiCl$	-5.605	-1.676	-4.278	-2.139
$LiBr$	-5.392	-1.718	-3.716	-1.858
LiI	-5.158	-1.763	-3.44	-1.72

εHOMO is eigen values of highest occupied molecular orbital; εLUMO is eigen values of lowest unoccupied molecular orbital, LUMO-HOMO is the energy gap, η is the absolute hardness calculated from equation - 7, DFT calculation have been made by DFT PW-91 method in conjunction with DZVP basis set on Cache Pro. Software

fect.

In the case of barium, calcium, strontium, magnesium, beryllium and lithium halides, the fluorides have the highest value on the scale of absolute hardness, and lowest in iodides. This sequence is perfect, and is as per established trends. The scale of hardness also demonstrates that sequence of hardness among the metal halides is as below.

$BeF_2 > MgF_2 > CaF_2 > SrF_2 > LiF > BaF_2$
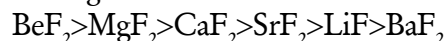
The same trend is shown by the softness values of Klopman, and also by the Log K values of the hydroxyl complexes[6]

Transition metal halides

The energies of HOMO and LUMO, the differences in their energies, and absolute hardness values of cobalt (II) halides and the halides of other transition metals as derived by DFT method are included in TABLE 3. Following observations are made from different values of this table

Unlike non transition metal halides, they do not furnish any trend. The highest value of hardness in case of manganese(II) halides is shown by $MnCl_2$ and lowest by MnF_2. In case of iron(II) halides and cobalt (II) halides, the hardness values are highest in their bromides and lowest in their selenocynate. The highest value of hardness in case of nickel(II) halides are shown by $Ni(NCSe)_2$ and in copper(II) halides by CuF_2. The lowest value in these two cases are respectively shown by NiF_2 and $Cu(NCSe)_2$. It is prominently demonstrated that absolute hardness values do not furnish any trend which may be compatible with established trend of hardness or softness. Scale of hardness if drawn by the value of IP and EA of previous work[6] or if the softness values $E_n \pm$ reported there are examined a clear trend of hardness is demonstrated. The fluorides of all the transition metal reported there are harder than other halides. The softest in all case is iodide. The trend among the metal is as below which is almost as per reported trend[27].

$Fe > Co > Ni > Cu$

Frontier molecular orbital densities

Molecular orbital energies are molecular properties whereas orbital densities are atomic properties, and provide useful information about donor acceptor interaction[18]. According to frontier electron re-

TABLE 3 : Absolute hardness value of transition metal halides, drawn from eigen values of HOMO and LUMO

Chemical sample	ε HOMO	ε LUMO	LUMO - HOMO	η
MnF_2	3.777	-0.325	4.102	2.051
$MnCl_2$	4.714	-0.208	4.92	2.461
$MnBr_2$	4.039	-0.873	4.912	2.456
MnI_2	4.211	-0.625	4.836	2.418
FeF_2	3.271	-1.572	4.843	2.4215
$FeCl_2$	5.382	0.835	4.547	2.2735
$FeBr_2$	4.641	-0.23	4.871	2.4355
FeI_2	4.262	-0.212	4.474	2.237
$Fe(NCS)_2$	-20.886	-23.966	3.08	1.54
$Fe(NCSe)_2$	-15.819	-17.562	1.743	0.8715
CoF_2	-7.275	-6.327	-0.948	0.474
$CoCl_2$	-6.894	-6.703	-0.191	0.0955
$CoBr_2$	2.539	0.392	2.147	1.0735
CoI_2	-5.185	-5.168	-0.017	0.0085
$Co(NCS)_2$	-0.863	1.942	1.079	0.5395
$Co(NCSe)_2$	-7.443	7.503	0.06	0.03
NiF_2	-7.227	-7.108	0.119	0.0595
$NiCl_2$	-6.386	-6.911	0.525	0.2625
$NiBr_2$	-5.955	-6.347	0.392	0.196
NiI_2	-5.559	-5.946	0.387	0.1935
$Ni(NCS)_2$	-4.685	5.784	1.099	0.5495
$Ni(NCSe)_2$	-5.708	8.06	2.352	1.176
CuF_2	-8.229	-2.414	-5.815	2.9075
$CuCl_2$	-7.295	-1.847	-5.448	2.724
$CuBr_2$	-6.798	-1.789	-5.009	2.5045
CuI_2	-6.307	-1.737	-4.57	2.285
$Cu(NCS)_2$	-6.159	-1.618	-4.541	2.2705
$Cu(NCSe)_2$	-14.023	-15.01	0.987	-0.4935

ε HOMO is eigen values of highest occupied molecular orbital, ε LUMO is eigen values of lowest unoccupied molecular orbital, LUMO-HOMO is the energy gap, and η is the absolute hardness calculated from equation 1.

TABLE 4: Highest HOMO density values of various donor molecules.

Compound	Atom	ρHOMO
CH_3NH_2	N	0.834
$(CH_3)_2NH$	N	0.754
$(CH_3)_3N$	N	0.695
$C_2H_5NH_2$	N	0.818
$(C_2H_5)_2NH$	N	0.738
$(C_2H_5)_3NH$	N	0.695
$PhNH_2$	N	0.354
Ph_2NH	N	0.325
Ph_3N	N	0.288
$HCONH_2$	O	0.793
CH_3CONH_2	O	0.798
$C_2H_5CONH_2$	O	0.778
$HCONHCH_3$	O	0.777
$C_6H_5CONH_2$	O	0.76
$PhCONH_2$	O	0.76
NH_2CONH_2	O	0.845
$CH_3NHCONH_2$	O	0.713
$PhNHCONH_2$	O	0.055
Ph_2NCONH_2	O	0.088
$(CH_3)_2NCON(CH_3)_2$	O	0.549
$CH_3NHCONHCH_3$	O	0.719
$HCSNH_2$	S	0.009
$HCSNCH_3$	S	0.009
$HCSNHC_2H_5$	S	0.257
$HCSN(C_2H_5)_2$	S	0.568
C_5H_4N	N	0.693
C_5H_4FN	N	0.21
C_5H_4ClN	N	0.023
C_5H_4BrN	N	0.026
C_5H_4IN	N	0.024

ρHOMO is the HOMO density calculated from DFT_PW91 method, in conjunction with DZVP basis on Cache software

activity theory, the chemical reaction takes place at a position where overlap of the HOMO and LUMO are the maximum[14]. In the case of donor molecule the HOMO density and in case of acceptor molecule the LUMO density are important for any reaction. Frontier orbital densities can strictly be used to describe the reactivity of different atoms in the same molecule[12,14]. The electron density of the HOMO at an atom is a measure of relative reactivity of the HOMO at that atom within a single molecule while the energy level of the HOMO reflects the reactivity of different molecule, thus molecules with smaller ionization potential (-ε HOMO) are expected to be more reactive as nucleophiles[19].

Nucleophiles

The HOMO densities of a number of donor molecules have been evaluated and the atom having the

highest density has been identified. The HOMO densities on such atoms are included in TABLE 4. It is evident that in all case of amides and ureas the highest density is shown at carbonyl oxygen. It has earlier been reported that amides and ureas coordinate through carbonyl oxygen[20, 21]. The highest HOMO density at carbonyl oxygen is in agreement with the experimental results. It is further indicated that in case of amides the highest density at carbonyl oxygen is observed in acetamide and lowest in benzamide the values are 0.798 and 0.76 respectively. In case of ureas the highest value of HOMO density is at carbonyl oxygen of urea, which is 0.845 and lowest at phenyl urea being 0.055. The trend shown by HOMO densities values is almost similar to the trend shown by HOMO energies and softness values.

The thioamide generally coordinate through thioamide sulphur[22], but in some cases, nitrogen has been shown as coordinating site[23]. The values of HOMO densities at various thioamide and thioureas are highest at sulphur as compared to other atoms. The highest value 0.568 is shown by diethyl thioformamide, and lowest value 0.009 by thioformamide. This supports the coordination through sulphur in thioamides.

In case of amines, and pyridine derivatives the high value of HOMO density is observed at nitrogen. In primary amines this value is higher as compared to secondary and tertiary amines, which is almost similar to the trend observed on the basis of HOMO energies and softness values of amines. In pyridine derivatives the highest value of HOMO density is shown at pyridine nitrogen and lowest at nitrogen of chloro pyridine.

Non transition metal halides

The HOMO-LUMO densities of metal atom in various halides are included in TABLE 5. The LUMO densities at M[M = Zn(II), Cd(II), Hg(II), Sn(IV)] are higher as compared to their HOMO densities. As expected they will be acceptors. The LUMO density is highest in case of fluorides and lowest in iodides. The LUMO density again rises in their thiocyanate and selenocyanate derivatives, indicating that in [M = Zn(II), Cd(II), Hg(II)] the thiocyanates and selenocyanates are better acceptors than their halide counterpart. The acceptor strength may also be cor-

related with the HOMO density of the compounds. The lower is the value better will be the acceptor property. In case of Sn(IV) halides, the highest LUMO density is exhibited by Sn(IV) chloride and lowest by Sn(IV) iodide. This is consistent with the experimental results [20, 21]. Amongst the methyl and phenyl substituted Sn(IV) halides the LUMO density at tin increases as the number of methyl substitution increases and in case of phenyl substitution the density decreases as the number of phenyl substitution increases. In case of Sn(IV) halides it is noticeable that their HOMO density is zero in all cases except in di and tri methyl substituted halides. This observation has a very good relation with the experimental observation. Sn(IV) halides have instantaneous reaction with even weak donor molecules[20, 21]

TABLE 5 : LUMO and HOMO desities on metal atoms of non-transition metal halides

Chemical Sample	Atom	ρLUMO	ρHOMO
ZnF_2	Zn	0.818	0.088
$ZnCl_2$	Zn	0.702	0.671
$ZnBr_2$	Zn	0.736	0.034
ZnI_2	Zn	0.644	0.025
$Zn(NCS)_2$	Zn	0.834	0.014
$Zn(NCSe)_2$	Zn	0.821	0.011
CdF_2	Cd	0.806	0.045
$CdBr_2$	Cd	0.729	0.026
$Cd(NCS)_2$	Cd	0.71	0.01
$Cd(NCSe)_2$	Cd	0.794	0.008
HgF_2	Hg	0.649	0.053
HgI_2	Hg	0.414	0.012
$Hg(NCS)_2$	Hg	0.621	0.01
$Hg(NCSe)_2$	Hg	0.649	0.078
$SnCl_4$	Sn	0.487	0
$SnBr_4$	Sn	0.411	0
SnI_4	Sn	0.293	0
$PhSnCl_3$	Sn	0.518	0
Ph_2SnCl_2	Sn	0.257	0
Ph_3SnCl	Sn	0.082	0
$(CH_3)SnCl_3$	Sn	0.52	0
$(CH_3)_2SnCl_2$	Sn	0.572	0.092
$(CH_3)_3SnCl$	Sn	0.688	0.09

ρLUMO is the LUMO density and ρHOMO is the HOMO density calculated from DFT_PW91 method, in conjunction with DZVP basis on Cache software

Transition metal halides

HOMO-LUMO densities of metal atom in various halides and their difference has been evaluated and are presented in TABLE 6.

The highest LUMO density is observed in the fluorides, the next is chloride in all the cases except cobalt where it is bromide. The lowest value is of thiocynates in the case of iron and cobalt, and selenocynate in the case of nickel and copper. It is evident that fluorides will be the best acceptor. The acceptor strength in the case of different fluorides is Fe-Co > Ni > Cu, whereas in other case it changes from halide to halide. HOMO-LUMO density difference does not indicate any worthwhile trend.

Metal-Ligand Interaction

TABLE 6 : HOMO and LUMO densities on metal atoms of transition metal halides.

Metal	Atom	ρLUMO	ρHOMO
FeF_2	Fe	0.999	0.06
$FeCl_2$	Fe	0.725	0.039
$FeBr_2$	Fe	0.255	0.04
FeI_2	Fe	0.129	0.047
$Fe(NCS)_2$	Fe	0.052	0.006
$Fe(NCSe)_2$	Fe	0.001	0.017
CoF_2	Co	0.999	0.815
$CoCl_2$	Co	0.568	0.816
$CoBr_2$	Co	0.983	0.055
CoI_2	Co	0.928	0.072
$Co(NCS)_2$	Co	0.367	0.155
$Co(NCSe)_2$	Co	-0.081	0.427
NiF_2	Ni	0.878	0.966
$NiCl_2$	Ni	0.604	0.686
$NiBr_2$	Ni	0.552	0.993
NiI_2	Ni	0.509	0.999
$Ni(NCS)_2$	Ni	-0.011	0.03
$Ni(NCSe)_2$	Ni	0.272	0.648
CuF_2	Cu	0.525	0.474
$CuCl_2$	Cu	0.368	0.314
$CuBr_2$	Cu	0.307	0.255
CuI_2	Cu	0.236	0.186
$Cu(NCS)_2$	Cu	0	0.158
$Cu(NCSe)_2$	Cu	0.122	0.144

ρLUMO is the LUMO density and ρHOMO is the HOMO density calculated from DFT_PW91 method, in conjunction with DZVP basis on Cache software

Parr and Yang[11] reconciled DFT with the frontier orbital theory of chemical reactivity. Since this theory is very successful we have applied the result of DFT calculations to metal-ligand interaction. The electron transfer between donor acceptor reactions involve definite filled orbitals on the donor and definite empty orbitals on the acceptors. The most important donor orbital will usually be the HOMO and the most important acceptor orbital will be the LUMO. The normalized electron densities of these frontier orbitals are called the fukui function-f [16].

f = çHOMO　　　donor molecule
f = çLUMO　　　acceptor molecule
f = 1/2 (çHOMO + çLUMO) both donor and acceptor.

The last equation is for the case where as electron transfers in both directions as in $\sigma + \pi$ bonding. The difference in energies of the HOMO of nucleophiles and LUMO of electrophiles has also been used to describe the stability of the bond formed between them[1,16,25]. In our recent communication we have shown that lower is the value of difference between the energy of HOMO and LUMO greater is the stability of the bond[24].

Based on the above principles we have made studies in various types of metal-ligand interaction as below.

Non transition metal halides

The difference in values of HOMO densities of a set of donor molecules and values of LUMO densities of a set of metal ions has been derived by the following equation

$\Delta LH = [çLUMO - çHOMO]$ and the results are tabulated in TABLE 7. in other words the difference in fukui function values of donor and acceptor molecules has been derived. The sequence of ΔLH in all the cases is as below
Ba > Ca > Sr > Li > Be > Mg

If lower ΔLH value is indicative of stable metal ligand bond magnesium is shown to form most stable bond and barium the least stable in the series. The log K values as reported earlier[26] also that magnesium forms more stable complexes than calcium, strontium and barium ions.

LUMO densities at M in M(II) thiocyanates [M = Zn, Cd, Hg] have been evaluated and HOMO densities of a set of organic donor molecules at the atom where the HOMO density is highest has been con-

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TABLE 7 :The HOMO density of ligands and LUMO density of certain non transition metal ions and their difference ΔLH =[LUMO-HOMO]

Ligand	Atom	ρ_{HOMO}	Li	Be	Sr	Ca	Mg	Ba
			ρ_{LUMO}	ρ_{LUMO}	ρ_{LUMO}	ρ_{LUMO}	ρ_{LUMO}	ρ_{LUMO}
			0.981	0.958	0.99	1.003	0.915	1.012
			ΔLH	ΔLH	ΔLH	ΔLH	ΔLH	ΔLH
Pyridine	N	0.693	0.288	0.265	0.297	0.31	0.222	0.319
Ethylenediamine	N	0.435	0.548	0.523	0.555	0.568	0.48	0.577
Nicotinamide	N	0.57	0.411	0.388	0.42	0.433	0.345	0.442
Tetrahyrofuran	O	0.687	0.294	0.271	0.303	0.316	0.228	0.325
Dimethylformamide	O	0.787	0.194	0.171	0.203	0.216	0.128	0.225
Triphenyl phosphine	P	0.523	0.458	0.435	0.467	0.48	0.392	0.489

ρLUMO is the LUMO density and ρHOMO is the HOMO density calculated from DFT-PW91 method, in conjunction with DZVP basis on Cache software

sidered for deriving ΔLH values. The ΔLH values are presented in TABLE -8. The ΔLH values clearly indicate that most stable complexes are formed by HgX_2[X = Cl, Br, I, SCN] when reaction takes place with pyridine nicotinamide triphenyl phosphine or pyridine oxide.

The LUMO densities at tin in its halides have been derived and HOMO densities at oxygen in ethylene urea and at sulphur in ethylene thiourea have been evaluated. The differences between the two densities indicate the following order of acceptor strength.
$SnCl_4 > SnBr_4 > SnI_4$
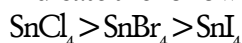
The ΔLH values are in total agreement with the results of ΔEnm[6] and also with the result derived by ΔN and ΔE values TABLE 10

Transition metal halides

The LUMO densities of M (II) halides (M = Fe, Co, Ni, Cu) and HOMO densities of pyridine and isoquinoline at their nitrogen ends are included in TABLE 9. The difference in their energies(ΔLH) does not provide any sequence, which may be well related with the experimental results or the established trend. The $f = 1/2(\varsigma HOMO + \varsigma LUMO)$, also does not provide any trend. The $\Delta E_{nm}\pm$ values derived by Klopman equation also did not provide any such sequence in earlier work[6], and a good relationship with experimental results could only be obtained after addition of CFSE values to $\Delta E_{nm}\pm$values. Similarly one more parameter will have to be added to ΔLH to obtain the required trend. Density functional theory or electron density alone could not describe all the chemical phenomena, its sensitivities of struc-

tural perturbation and responses to changes in external condition are rather more important[27]. In the light

TABLE 8 : LUMO densities of acceptor M-halides [M = Sn(IV), Zn(II), Cd(II), Hg(II)] and HOMO density of donor and the difference ΔLH in LUMO-HOMO densities

Compound	ΔE_{nm}?	ρ_{LUMO}	ρ_{HOMO}	ΔLH
$SnCl_4.2EU$	27.14	0.487	0.778	0.291
$SnBr_4.2EU$	25.41	0.411	0.778	0.367
$SnI_4.2EU$	23.37	0.293	0.778	0.485
$SnCl_4.2ETU$	25.74	0.487	0.909	0.422
$SnBr_4.2ETU$	24.07	0.411	0.909	0.498
$SnI_4.2ETU$	21.97	0.293	0.909	0.616
$SnCl_4.2ATU$	26.04	0.487	0.89	0.403
$SnBr_4.2ATU$	24.29	0.411	0.89	0.479
$SnI_4.2ATU$	22.25	0.293	0.89	0.597
$Zn(NCS)_2.2PY$	4.22	0.834	0.693	0.141
$Cd(NCS)_2.2PY$	3.22	0.71	0.693	0.017
$Hg(NCS)_2.2PY$	2.07	0.621	0.693	0.072
$ZnCl_2.2nia$	7.03	0.702	0.57	0.132
$CdCl_2.2nia$	6.05	0.752	0.57	0.182
$HgCl_2.2nia$	5.18	0.539	0.57	0.031
$ZnCl_2.2PPh_3$	0	0.702	0.525	0.177
$CdCl_2.2PPh_3$	0.98	0.752	0.525	0.227
$HgCl_2.2PPh_3$	1.85	0.539	0.525	0.014
$ZnCl_2.2PYO$	6.21	0.702	0.537	0.165
$CdCl_2.2PYO$	5.23	0.752	0.537	0.215
$HgCl_2.2PYO$	4.36	0.539	0.537	0.002

ρLUMO is LUMO density and ρHOMO is the HOMO density and ΔLH is their difference calculated from DFT-PW91 method, in conjunction with DZVP basis on Cache Pro software. The ΔEnm??++ is difference in softness values of metal halides and donor molecules (6).

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of the above we tried other parameters, which in combination with ΔLH could provide a proper trend in studying the transition metal reactions. Ionization potential evaluated by the method described else where[2] provided the solution. If values of IP of the Lewis acids are added to the value of ΔLH, the following trend in stability of metal ligand bond is obtained which is similar to the order reported on the basis of thermodynamic stability (log K) of transition metal complexes[28].

Cu>Ni>Co>Fe.

Charge transfer ΔN and energy lowering ΔE

There has been a number of molecular orbital treatments of Lewis acid-base reaction. The Mulliken[26] treatment has been recognized as best for donor acceptor interaction in charge transfer complexes. This theory uses only electron affinity A_A for acceptor and only ionization potential I_B for the elec-

TABLE 9 : LUMO densities and IP of transition metal halides and HOMO densities of pyridine and isoquinoline

Compounds	ρ_{LUMO}	ρ_{HOMO}	IP	ΔLH	ΔLH+IP
$Fe(py)_4Cl_2$	0.725	0.693	20.11	0.032	20.142
$Fe(py)_4Br_2$	0.255	0.693	19.28	-0.438	18.842
$Fe(IQ)_4Cl_2$	0.725	0.032	20.11	0.693	20.803
$Fe(IQ)_4Br_2$	0.255	0.032	19.28	0.223	19.503
$Fe(IQ)_4I_2$	0.129	0.032	17.84	0.097	17.937
$Co(py)_4Cl_2$	0.568	0.693	21.23	-0.125	21.105
$Co(py)_4Br_2$	0.983	0.693	20.2	0.29	20.49
$Co(IQ)_4Cl_2$	0.568	0.032	21.23	0.536	21.766
$Co(IQ)_4Br_2$	0.983	0.032	20.2	0.951	21.151
$Co(IQ)_4I_2$	0.928	0.032	18.65	0.896	19.546
$Ni(py)_4Cl_2$	0.604	0.693	22.27	-0.089	22.181
$Ni(IQ)_4Cl_2$	0.604	0.032	22.27	0.572	22.842
$Ni(IQ)_4Br_2$	0.552	0.032	21.29	0.52	21.81
$Ni(IQ)_4I_2$	0.509	0.032	19.57	0.477	20.047
$Cu(py)_4Cl_2$	0.368	0.693	27.24	-0.325	26.915
$Cu(py)_4Br_2$	0.307	0.693	26.27	-0.386	25.884
$Cu(py)_4I_2$	0.236	0.693	24.36	-0.457	23.903
$Cu(IQ)_4Cl_2$	0.368	0.032	27.34	0.336	27.676
$Cu(IQ)_4Br_2$	0.307	0.032	26.27	0.275	26.545
$Cu(IQ)_4I_2$	0.236	0.032	24.36	0.204	24.564

ρ_{LUMO} is LUMO density, ρ_{HOMO} is HOMO density and ΔLH is their difference calculated from DFT-PW91 method, in conjunction with DZVP basis on Cache Pro software. IP is the ionization potential of an atom in molecule (2).

tron donor. The quantity (I_B-A_A) is an energy cost of transfer of per electron for donor to acceptor to decide which of the two molecules is donor and which is acceptor, we have the following equation-

$$(I_A-A_B) - (I_B-A_A) = 2(\chi_A^0 - \chi_B^0) \qquad (10)$$

A positive value indicates that it cost less energy to transfer an electron from B to A. Thus the direction of electron transfer is determined by the absolute electronegativity and the magnitude is the deriving force for electron transfer. The absolute electronegativity of acceptor (A) and donors (B) are included in TABLE 10. A lower value of electronegativity is indicative of a better donor character whereas a higher value of electronegativity is indicative of a better acceptor character[10]. A reference to the table indicates that electronegativity values of donor mol-

TABLE 10 : The absolute hardness and electronegativity of acid (A) and bases (B) and ΔE and ΔN derived from them

Potential Compounds		A		B		ΔE	ΔN
A	B	η	χ	η	χ		
$SnCl_4$	EU	1.7930	6.2930	2.9665	2.6265	0.7061	0.3852
$SnBr_4$	EU	1.4640	5.8060	2.9665	2.6265	0.5704	0.3588
SnI_4	EU	1.0690	5.4280	2.9665	2.6265	0.4862	0.3471
$SnCl_4$	ETU	1.7930	6.2930	1.8720	2.6280	0.9163	0.5000
$SnBr_4$	ETU	1.4640	5.8060	1.8720	2.6280	0.7569	0.4763
SnI_4	ETU	1.0699	5.4280	1.8720	2.6280	0.6664	0.4760
$SnCl_4$	ATU	1.7930	6.2930	1.6905	2.8625	0.8446	0.4924
$SnBr_4$	ATU	1.4640	5.8060	1.6905	2.8625	0.6867	0.4646
SnI_4	ATU	1.0690	5.4280	1.6905	2.8625	0.5963	0.4648
$Zn(NCS)_2$	Py	1.7930	4.2500	2.0830	3.7160	0.0172	0.0645
$Cd(NCS)_2$	Py	1.4640	4.6840	2.0830	3.7160	0.0668	0.1381
$Hg(NCS)_2$	Py	1.0690	4.7400	2.0830	3.7160	0.0731	0.1427
CdF_2	nia	2.0575	5.5774	1.8085	3.9335	0.1635	0.1989
HgF_2	nia	1.4225	6.5100	1.8085	3.9335	0.4383	0.3402
CdF_2	PPh₃	1.5045	5.5774	1.8040	3.2250	0.3351	0.2849
HgF_2	PPh₃	2.3247	6.5100	1.8040	3.2250	0.7131	0.4342
CdF_2	PyO	1.9779	5.5774	1.5440	3.6070	0.2509	0.2547
HgF_2	PyO	2.3247	6.5100	1.5440	3.6070	0.5980	0.4120

η and χ are the absolute hardness and electronegativity of acid A and base B. ΔN is the shift in charge calculated from equation 4 and ΔE is energy lowering calculated from equation 5 by using DFT-PW91 method, in conjunction with DZVP basis on Cache Pro software. The EU is ethylene urea, ETU is ethylene thiourea, ATU is alkyl thio urea, Py is pyridine, nia is nicotinamide, PPh3 is tri phenyl phosphine, PyO is pyridine oxide.

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ecules are less than that of acceptor molecules hence the equation 10 has a positive value. The values indicated that the acceptor strength of Sn(IV) halides will be $SnCl_4 > SnBr_4 > SnI_4$ and in case of Zn, Cd and Hg halides, the Hg halides will be the best acceptor when react with donor molecules. On the basis of χ values the base strength of donor molecules can be arranged as below.
EU>ETU>ATU>PPh3>PyO>Py>NIA

The electronegativity(χ) difference derives the electron transfer and the sum of hardness parameters(η) inhibits it. The net result of shift in charge ΔN and lowering in energy ΔE due to electron transfer is given by the equation 5 and 6. The values of ΔN and ΔE have been evaluated and are reported in TABLE 10. The DN values clearly indicate that maximum charge transfer is in $SnCl_4$ complexes of EU, ETU and ATU and minimum in case of SnI_4 complexes. Similarly $SnCl_4$ complexes exhibited the maximum energy lowering. In case of Zn, Cd and Hg complexes the maximum values of ΔN and ΔE are observed in case of Hg complexes. All the results are in conformity with the results obtained by ΔLH values and ΔE_{nm} values[6].

Multiple linear regression

DFT calculations provide a method by which value of absolute hardness, electronegativity, chemical potential, ΔE, ΔN etc can be calculated reliably. However the computer takes much time for DFT calculations, and is accordingly expensive. There is thus a need to establish reliable procedures for predicting the absolute hardness value of chemicals from the knowledge of such properties, which are readily measurable. The most common approach is multiple linear regression (MLR) analysis. This method attempts to model the relationship between two or more explanatory variable and a response variable by fitting a linear equation to observed data. The general regression equation can be written as:

$Z = ax + by + c$ (11)

The constants a, b and c in the regression equation are called regression coefficients and given by the following equations-
$\Sigma z = a\Sigma x + b\Sigma y + Nc$
$\Sigma xz = a\Sigma x^2 + b\Sigma y + c\Sigma x$
$\Sigma yz = a\Sigma xy + b\Sigma y^2 + c\Sigma y$

Where N is the number of data used.

When values of a, b and c are found, the regression equation can be written using these values. The regression line is the equation of the line of best fit for the data available to us. In other words the error, which is the vertical distance of each of the points from the regression line, is the smallest using this line.

In our present work we have evaluated absolute hardness values of certain amides, ureas, their thio counterpart and derivatives of pyridine, with the help of ionization potential and electron affinity values, obtained by DFT B88LYP calculations. With the help of these values the absolute hardness (η) values have been calculated and the results are given in TABLE - 11. The value of hardness (η) is the observed data that is z of equation-11. The two descriptors x and y are ionization potential and electron affinity, which have been taken from reference[6] but are also readily measurable by the method described in that reference. The MLR equation has been built up as below-

Observed value of hardness obtained by DFT B88LYP method
Des 1 = IP as first descriptor
Des 2 = EA as second descriptor
Pred = Value of hardness predicted by MLR by the formula
Pred = 0.180477*(Descriptor IP)-0.0998659*(Descriptor EA)-1.58952
$RCV^2 = 0.934896$ $r^ = 0.94267$

The predicted values and values of coefficient have been evaluated. The model of relationship between DFT based η values, and the predicted values are reliable as the values of linear coefficient r^2 and cross validation coefficient rCV^2 are 0.94267 and 0.9248. MLR analysis has widely been used in medicinal chemistry for QSAR modeling of drugs[28], and also for bio-concentration factor which is an important eco-toxicological parameter[27]. The MLR analysis in respect of reactivity of a compound based on hardness parameter is first of its kind.

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TABLE 11 : DFT based absolute hardness, obtained from IP and EA value. Predicted values obtained by EA and IP values of reference(6)

No.	Compd.	DFT(IP)	DFT(EA)	obs(η =(IP-EA)/2	Des.1 IP	Des. 2 EA	η = (IP-EA)/2	Pred. (η) = (IP-EA)/2	Residual
1	PhNH$_2$	4.634	0.781	1.927	26.74	12.16	7.29	2.022	-0.095
2	(Ph)$_2$NH	4.697	1.237	1.730	26.71	12.13	7.29	2.02	-0.29
3	HCONH$_2$	5.854	0.548	2.653	28.95	9.05	9.95	2.732	-0.079
4	CH$_3$CONH$_2$	5.616	0.355	2.631	28.38	8.63	9.88	2.671	-0.04
5	C$_2$H$_5$CONH$_2$	5.616	0.326	2.645	28.08	8.42	9.83	2.637	0.007
6	HCONHCH$_3$	5.784	0.474	2.655	28.38	8.63	9.88	2.671	-0.015
7	(CH$_3$)$_2$NCON(CH$_3$)$_2$	4.972	-0.549	2.761	27.92	8.3	9.81	2.621	0.14
8	HCSNH$_2$	4.993	1.901	1.546	22.5	9.43	6.54	1.529	0.017
9	HCSNHCH$_3$	4.878	1.84	1.519	22.31	9.21	6.55	1.517	0.002
10	HCSN(CH$_3$)$_2$	4.714	1.677	1.519	22.21	9.1	6.56	1.51	0.008
11	HCSNHC$_2$H$_5$	4.824	1.791	1.517	22.21	9.1	6.56	1.51	0.006
12	HCSN(C$_2$H$_5$)$_2$	4.424	1.454	1.485	22.1	8.98	6.56	1.502	-0.017
13	C$_5$H$_5$N	5.964	1.79	2.087	25.52	9.44	8.04	2.074	0.013
14	C$_5$H$_4$FN	6.612	2.065	2.274	27.13	12.73	7.20	2.036	0.238
15	C$_5$H$_4$ClN	6.526	2.128	2.199	27.24	12.57	7.34	2.071	0.128
16	C$_5$H$_4$BrN	6.358	2.132	2.113	27.13	12.49	7.32	2.06	0.053
17	C$_5$H$_4$IN	6.069	2.14	1.965	26.92	12.3	7.31	2.041	-0.076

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